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NASA TTF-10,275

N66 36136
(ACCESSION NUMBER)
32
(PAGES)
(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

06
(CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON D.C.   AUGUST 1966

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ABSTRACT

A theory of the interaction of atoms adsorbed on /734*

a metal surface is constructed. The relationship of

the tungsten work function, calculated by means of this

theory, to the degree of covering $\Delta\phi(\Theta)$ by its adsorbed

atoms and the change in heat of adsorption are in good

agreement with those experimentally measured for Ba-W

(Ref. 1) and Cs-W (Ref. 2) systems. A criterion is

formulated for determining the number of adsorbed atoms

in the monolayer.

INTRODUCTION

Part I of this work (Ref. 1), carried out together with Yu. S. Veluda,

set forth the results of experimental research on Ba and BaO adsorption .

on tungsten. Part I demonstrated that adsorption heat q of Ba and BaO

is strongly dependent on the degree Θ to which the tungsten surface is

covered with adsorbed atoms (adatoms) or molecules. It was found that the

relationship $\delta q(\Theta) = q_0 - q(\Theta)$, where q_0 is the heat of adsorption

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* Note: Numbers in the margin indicate pagination in the original foreign
text.

when $\theta = 0$, is described by formula

$$\delta q(\theta) = \frac{a\theta}{1+b\theta} + (q_0 - q_1 - L)\left\{\frac{1-\theta}{[1-0.99\theta(2-\theta)]^{\frac{1}{3}}}\right\},$$ (1)

where a = 3.6 ev, b = 1.25, $q_1 = \frac{a}{1+b}$, and L is the latent heat of vapor-
ization of a substance which vaporizes from its own crystal. Expression (1)
is true not only for the Ba-W and BaO-W systems which we studied, but also
for the Cs-W system studied by Taylor and Langmuir (Ref. 2). Values of
q_0 were also obtained for these systems. It was moreover also demonstrated
that the following equation

$$-\frac{d\theta}{dt} = \frac{kT}{h}\theta e^{-\frac{q(\theta)}{kT}}$$ (2)

from the theory of absolute reaction velocities (Ref. 3), k here being
Boltzmann's constant and h, Planck's constant, together with equation (1)
satisfactorily describe the isobars and dynamic isotherms of desorption
which were experimentally measured.

The literature contains a number of works conducting a theoretical
analysis of the change in the heat of atom and molecule adsorption on metals
accompanying the change in θ. These works attempt to explain this change
in adsorption heat with the change in θ principally from two points of view.
According to the first point of view, (Refs. 4, 5) the heat is decreased
because of superficial unevenness. On a nonuniform surface the most active
centers are first filled and adsorption heat continuously decreases.
Unfortunately, this hypothesis has not been numerically formulated, and
it can moreover hardly explain the great changes in adsorption   /735
heat (see [Ref. 6], for example).

According to the second view, which was enunciated by Roberts (Ref. 7), adsorption heat may be reduced by repulsion forces which act between the atoms or molecules in the adsorption layer. Assuming that these forces are electrostatic in origin, Roberts computed $\delta q(\theta)$ for a system of dipoles on metal (Langmuir's model) (Ref. 7). It was found, however, that the experimetally determined $\delta q(\theta)_{exp}$ is several times larger than the theoretically derived $\delta q(\theta)_{theor}$.

Higuchi, Reid, and Eyring (Ref. 8) computed $\delta q(\theta)$ for a system of polarized ions on metal (known as the De-Boer model). The agreement between $\delta q(\theta)_{exp}$ and $\delta q(\theta)_{theor}$ obtained by the authors was reached only by artificial selection of the theoretical parameter. The expression which they obtained for $\delta q(\theta)$ with low values of θ is, moreover, incorrect since in their work the equation $\delta q(\theta) = 0$ has still another root $\theta_m > 0$, in addition to the root $\theta = 0$. The result of this is that $\delta q(\theta)$ in the $0 < \theta < \theta_m$ range has a sign opposite to that which this variable has when $\theta > \theta_m$, which contradicts experimental experience.

Therefore, it follows from the data in the literature that neither the first nor the second mechanism explains the great changes in adsorption heat (on the order of 2 to 4 ev) which are observed in experiment. De-Boer has recently attempted to surmount these difficulties by associating the change in adsorption heat with the change in the work function (Refs. 9,10).

This paper has endeavored to explain the role of the electrostatic interaction of adatoms among themselves in the changes in work function and adsorption heat during a change in the degree of covering during

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adsorption of Ba and BaO on a tungsten surface, as was observed in

(Ref. 1), and also to clear up certain other matters. We have assumed

that the change in q when $\theta \lesssim 0.5$ and when $\theta > 0.5$ is caused by different

mechanisms. When $\theta \lesssim 0.5$ the change in q is caused by electrostatic

interaction of the adatoms with all the others. When $\theta > 0.5$ we may connect the

drastic heat reduction in the case of the Ba-W and Cs-W systems to elec-

trostatic interaction of adjacent atoms which, because of their statistical

distribution on the surface, approach each other at a distance less than

the minimum distance between them in a monomolecular layer.

Electrostatic Interaction Of Adsorbed Atoms and Molecules on a Metal Surface

Let us assume that the dependence found in (Ref. 1) of the change in

the work function on covering degree $\Delta\phi(\theta)$ and $q(\theta)$ when $\theta \lesssim 0.5$ is first

of all associated with the electrostatic interaction among adsorbed atoms

and molecules. We shall not take surface nonuniformity into consideration,

i.e., we shall assume that the surface is uniform.

Examination of Possible Models of the Effect. When atoms and molecules

are adsorbed, a change is usually observed in the work function of an

electron from the substratum. Two models have been proposed to explain

this effect and the appearance of the $\Delta\phi(\theta)$ curves. The first, proposed

by Langmuir (Ref. 11), posits polarized adatoms (Figure 1a); the second,

proposed by De-Boer (Ref. 12) is based on the assumption that the adatoms

are ionized with subsequent polarization of the ions by an electric field

(dipoles P_1). The ions and their mirror images form dipoles P_0 (Figure 1b).

Both models take into consideration the mirror images of the ions and
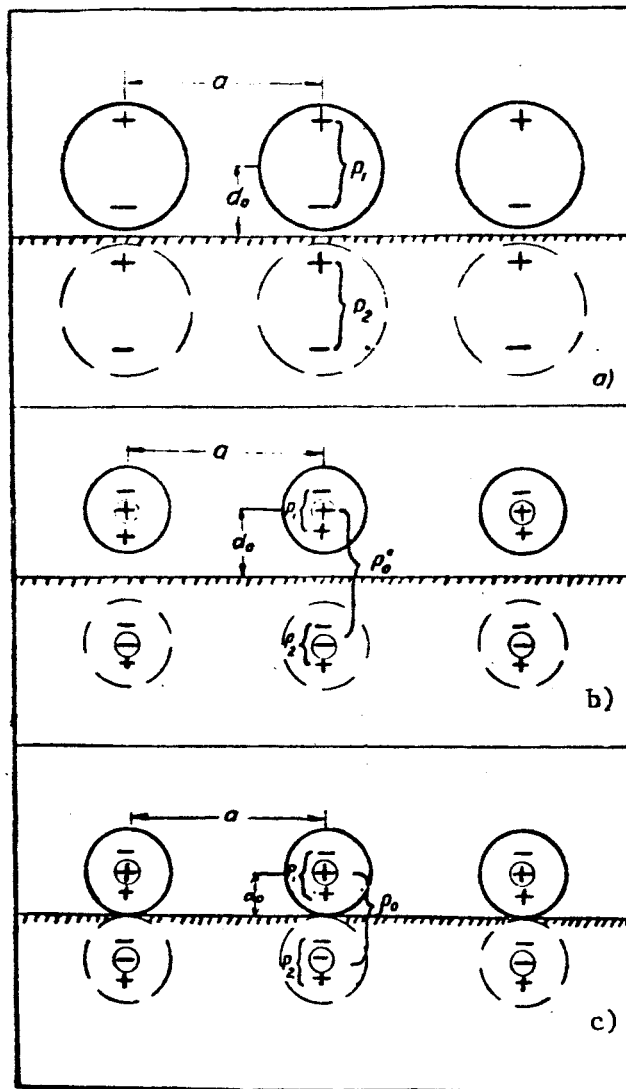
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Figure 1

the dipoles in the metal substratum. The De-Boer model considers dipole P_0 to be rigid, which can hardly be supported. We will examine a model in which dipole P_0 is soft and, additionally, we will regard the degree of ionization γ to be arbitrary. This general model includes both the /736 De-Boer model and the Langmuir model. Therefore, it is sufficient to calculate $\Delta\phi(\Theta)$ and $\delta q(\Theta)$ for our model and to simultaneously calculate these values also for the two above-mentioned models.

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Calculating the Effective Field. On the metal surface let us assume

there is a monomolecular layer of adatoms which forms a two-dimensional square

or hexagonal lattice whose constant is a. Let us compute the normal effective

composite electrical field which acts in the center of an arbitrary adatom

from the direction of the other adatoms, i.e., from the direction of all

the ions and their mirror images, as well as from the direction of all

dipoles P_1 and P_2 (Figure 1c). We will consider the desired field $\mathcal{E}$ to

be equal to the sum of the fields of all dipoles P_0, P_1, and P_2 which act

at the given point, as well as of the fields of the ion mirror image and of

dipole P_1. Let us assume that the field of the ions and their mirror

images may be replaced by the field of dipoles P_0. Therefore, <u>/737</u>

$$\mathcal{E} = \frac{C_0}{a^3} P_0 - \frac{C_1}{a^3} P_1 - \frac{C_2}{a^3} P_2 + \frac{P_1}{4d^3} + \frac{\gamma e}{4d^2},$$ (3)

where γe is the ion charge, d is the distance of the ion from the metal

surface, and

$$C_0 = - \sum_{m=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \frac{2\frac{d^2}{a^2} - (m^2 + l^2)}{\left(\frac{d^2}{a^2} + m^2 + l^2\right)^{\frac{5}{2}}}, \quad C_1 = 9,0336 \, [7], C_2 = - \sum_{m=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \frac{8\frac{d^2}{a^2} - (m^2 + l^2)}{\left(4\frac{d^2}{a^2} + m^2 + l^2\right)^{\frac{5}{2}}}$$ (4)

for a square lattice and

$$C_0 = - \sum_{m=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \frac{2\frac{d^2}{a^2} - (m^2 - ml + l^2)}{\left(\frac{d^2}{a^2} + m^2 - ml + l^2\right)^{\frac{5}{2}}}, \quad C_1 = 8,8927 \, [7],$$

$$C_2 = - \sum_{m=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \frac{8\frac{d^2}{a^2} - (m^2 - ml + l^2)}{\left(4\frac{d^2}{a^2} + m^2 - ml + l^2\right)^{\frac{5}{2}}}$$

for a hexagonal lattice.

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In these sums m and 1 are whole numbers which do not simultaneously equal zero. Figure 2 gives a curve for finding the value of the sums of C_2 and C_0 depending on the parameter $(d/a)^2$ for the square lattice case.

We now compute that

$$P_0 = P_0^0 - \beta\mathscr{E}; \; P_1 = P_2 = P_1^0 + \alpha\mathscr{E}; \; d = d_0\left(1 - \frac{\beta\mathscr{E}}{2\gamma ed_0}\right); \; C \rightarrow C_1 + C_2, \qquad (5)$$

where α and β are the polarized states of dipoles P_1 and P_0, respectively; P_1^0, $P_0^0 = 2\gamma ed_0$, d_0 are the moments of these dipoles and the distance of the ion from the surface when $\Theta = 0$, i.e., when there are no adatoms but the one in question on the surface. Then we have

$$\mathscr{E} = \frac{C_0}{a^3}(P_0^0 - \beta\mathscr{E}) - \frac{C}{a^3}(P_1^0 + \alpha\mathscr{E}) +$$

$$+ \frac{P_1^0 + \alpha\mathscr{E}}{4d_0^3\left(1 - \frac{\beta\mathscr{E}}{2\gamma ed_0}\right)^3} + \frac{\gamma e}{4d_0^2\left(1 - \frac{\beta\mathscr{E}}{2\gamma ed_0}\right)^2}. \qquad (6)$$

In the case where $\dfrac{\beta\mathscr{E}}{2\gamma ed_0} \ll 1$ each of the two last terms in (6) may be expanded in series and restricted to terms which contain $\mathscr{E}$ to a degree no higher than the first. The sums in (4) contain /738 terms no higher than zero degree. We then obtain

$$\mathscr{E} \approx \frac{C_0}{a^3}(P_0^0 - \beta\mathscr{E}) - \frac{C}{a^3}(P_1^0 + \alpha\mathscr{E}) + \frac{\alpha\mathscr{E}}{4d_0^3} + \frac{3\beta\mathscr{E}}{4d_0^3}\frac{P_1^0}{P_0^0} + \frac{\beta\mathscr{E}}{4d_0^3} + \frac{P_1^0}{4d_0^3} + \frac{\gamma e}{4d_0^2}. \qquad (7)$$

It is found that $2\gamma ed_0 = P_0^0$.

We should mention that the last two items in (7) comprise the field $\mathscr{E}_0$ which also acts in the center of the adatom when it alone is found on the surface, i.e., when $\Theta = 0$. It is obvious that this value does not

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depend on Θ, i.e., on the presence of other adatoms. Since in the following we will be interested only in that part of the electric field which depends on Θ, we will, after making the substitution $E = \mathscr{E} - \mathscr{E}_0$, in (7), obtain

$$E = \frac{C_0 P_0^0 - C P_1^0}{a^3 f (1 + b)},$$ (8)

where

$$f = 1 - \frac{\alpha + \beta + 3\beta \frac{P_1^0}{P_0^0}}{4 d_0^3}; \quad b = \frac{C\alpha + C_0 \beta}{a^3 f}.$$ (9)

The energy of interaction of dipole P_1 with field E, which belongs to a single adatom will, taking expressions (8) and (5) into account, be

$$U_1 = -\frac{1}{2} P_1 E + \frac{1}{2} \alpha E^2 = -\frac{1}{2} P_1^0 E =$$
$$= -\frac{P_1^0 (C_0 P_0^0 - C P_1^0)}{2 a^3 f (1 + b)}.$$ (10)

The energy of interaction of an ion with field E, which belongs to a single adatom, may be defined as half the energy of interaction of dipole P_0 with this field, since at the points where the ion and its mirror image are located (in case there is no metal) the potential values of field E are equal and opposite in sign. Therefore, we have

$$U_2 = \frac{1}{2} \frac{1}{2} P_0^0 E = \frac{P_0^0 (C_0 P_0^0 - C P_1^0)}{4 a^3 f (1 + b)}.$$ (11)

Thus, the energy of an adatom in field E will be

$$U = U_1 + U_2 = \frac{(P_0^0 - 2 P_1^0)(C_0 P_0^0 - C P_1^0)}{4 a^3 f (1 + b)}.$$ (12)
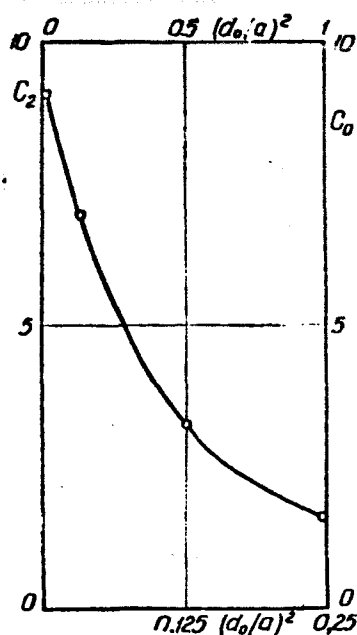
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Figure 2

Transition to an Arbitrary Degree of Covering. In the following

we will examine two cases: localized and unlocalized adsorption (e.g.,

see [Ref. 6]). In the first case, the adatoms are at distances one from

another which are divisible by the lattice constant of the substratum,

i.e., their arrangement is determined by the topography of the sub-

stratum. In the second case, the average distance between adatoms may

change continuously with a change in degree of covering, i.e., the

potential topography of the substratum has no effect on adatom distri-

bution. For the mobile film with no interadatom repulsion, in the first

case the adatoms are usually randomly distributed among the potential holes /739

on the surface of the metal, while in the second case they are distributed

randomly over its surface. When repulsion is present, in the first case

with low and high degrees of covering the distribution will be almost random,

while with medium degrees of covering it perceptibly deviates from this.

In the second case, the distribution will be uniform.

In order to make the transiton from monomolecular covering ($\theta = 0$) in expressions (8) and (12) to a firm with arbitrary degree of covering, the relationship of C and C_0 to θ must be found. In different cases, this dependence will vary. It is simplest to describe this dependence for the case of unlocalized adsorption where there is mutual repulsion between adatoms (uniform adatom distribution). In this case, in order to make the transition from an arbitrary degree of covering it is sufficient to make the substitution $a = \dfrac{1}{\sqrt{n_1 \theta}} = \dfrac{a_1}{\sqrt{\theta}}$, everywhere, where n_1 is the number of adatoms in the monolayer per sq. cm of surface and a_1 is the monolayer lattice constant. As a result, we will arrive at expressions in which C and C_0 will be functions of θ. This is very inconvenient for computations. It can be readily found that there will be no great error if we replace these variables by their average values as θ changes from zero to unity. Then we have

$$E(\theta) \approx \frac{(\bar{C}_* P_0^0 - \bar{C} P_1^0)\theta^{\frac{3}{2}}}{a_1^3 f (1 + \bar{b}\theta^{\frac{3}{2}})}, \quad U(\theta) \approx \frac{(P_0^0 - 2P_1^0)(\bar{C}_0 P_0^0 - \bar{C} P_1^0)\theta^{\frac{3}{2}}}{4 a_1^3 f (1 + \bar{b}\theta^{\frac{3}{2}})}. \tag{13}$$

According to Roberts and Miller (Ref. 13), in the case of localized adsorption the transition from an arbitrary degree of covering may be satisfactorily made by simply multiplying C and C_0 by θ everywhere. It must, however, be mentioned that this conversion is valid only in the case where the mutual repulsion of adjacent adatoms may be neglected. And, in fact, if there is no repulsion, the adatoms will be randomly distributed over the potential holes of the surface. Then each atom will have an average of

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$N_1\theta$ first neighbors, $N_2\theta$ second neighbors, and so on, i.e., the sums of C and C_0 are simply reduced θ times. The same will also be true in the case of unlocalized adsorption if there is no repulsion. When there is perceptible repulsion, there will be fewer immediate neighbors than $N_1\theta$ or $N_2\theta$, etc., since as the result of mutual repulsion these adatoms will seek to transfer into more distant potential holes. Therefore, we will obtain approximately

$$E(\theta) \approx \frac{(C_\bullet P_0^0 - C P_1^0)\,\theta}{a^3 f (1 + b\theta)}\,, \quad U(\theta) \approx \frac{(P_0^0 - 2P_1^0)(C_\bullet P_0^0 - C P_1^0)\,\theta}{4a^3 f (1 + b\theta)} \tag{14}$$

for localized adsorption when there is repulsion.

Computing $\delta q(\theta)$. From expression (13) we obtain

$$\delta q(\theta) = \frac{\partial U \cdot n_1 \theta}{\partial (n_1 \theta)} = \frac{(P_0^0 - 2P_1^0)(\bar{C}_\bullet P_0^0 - \bar{C} P_1^0)\,\theta^{\frac{3}{2}}\left(\frac{5}{2} + \bar{b}\theta^{\frac{3}{2}}\right)}{4a_1^3 f (1 + \bar{b}\theta^{\frac{3}{2}})^2} \tag{15}$$

for the case of unlocalized adsorption. From expression (14) we find that

$$\delta q(\theta) = \frac{\partial U \cdot n_1 \theta}{\partial (n_1 \theta)} = \frac{(P_0^0 - 2P_1^0)(C_\bullet P_0^0 - C P_1^0)\,\theta\,(2 + b\theta)}{4a^3 f (1 + b\theta)^2}\,. \tag{16}$$

for localized adsorption. Setting $\beta = 0$ in expressions (15) and (16), we derive the expression for $\delta q(\theta)$ for De-Boer's model which differs substantially from that obtained by Higuchi et al. (Ref. 8) for this model. /740 In addition, by setting $P_0^0 = 0$ in expressions (15) and (16), we derive the corresponding expressions for Langmuir's model.

Computing $\Delta\delta(\theta)$. To calculate $\Delta\delta(\theta)$ we use the familiar expression

$$\Delta\varphi(\theta) = -4\pi n_1 P_{\text{eff}}\theta, \tag{17}$$

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where P_{eff} is the effective dipole moment per adatom. The minus sign indicates that the work function decreases when the moment of the double layer is positive.

The literature contains confirmation (Ref. 10) of the fact that expression (17) may be used only in the case where the charge which creates the double layer is diffuse. When, however, the charges are discretely distributed, (17) is invalid. But this is not so. We will show that (17) is also valid in the case of discrete charge distribution. In our case, in fact, $\Delta\varphi = \int\limits_0^{\infty} E(x)\,dx.$, where $E(x)$ is the normal component of the electric field. On the other hand, it is easy to ascertain that for a square lattice, for example,

$$E(x) = \frac{P_0 - 2P_1}{a^3} \sum_{m=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \frac{2\frac{x^2}{a^2} - (m^2 + l^2)}{\left(\frac{x^2}{a^2} + m^2 + l^2\right)^{\frac{5}{2}}}, \tag{18}$$

Therefore, we have

$$\Delta\varphi(\theta) = -\frac{2P_{e\phi}}{a^2} \sum_{m=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \frac{\frac{z}{a}}{\left(\frac{z^2}{a^2} + m^2 + l^2\right)^{\frac{3}{2}}}, \tag{19}$$

since $P_0 - 2P_1 = 2P_{eff}$.

The double sum in (19) may be approximated in the form

$$\sum \sum \approx 4 \left\{ \sum_{m=0}^{N} \sum_{l=0}^{N} \frac{\frac{z}{a}}{\left(\frac{z^2}{a^2} + m^2 + l^2\right)^{\frac{3}{2}}} + \frac{z}{a} \int\limits_0^{\frac{\pi}{2}} \int\limits_N^{\infty} \frac{r\,dr\,d\varphi}{\left(r^2 + \frac{z^2}{a^2}\right)^{\frac{3}{2}}} \right\} = \tag{20}$$

$$= \frac{4z}{a} \left\{ \sum_0^{N} \sum_0^{N} \frac{1}{\left(\frac{z^2}{a^2} + m^2 + l^2\right)^{\frac{3}{2}}} + \frac{\pi}{2\left(N^2 + \frac{z^2}{a^2}\right)^{\frac{1}{2}}} \right\}.$$

Now let $z \to \infty$. Then the double sum will approach 2π and we will have

$$\Delta \varphi (\Theta) = -\frac{2P_{\text{eff}}}{a^3} 2\pi = -4\pi n_1 P_{\text{eff}} \Theta, \tag{17a}$$

since $a^2 = \dfrac{1}{n_1 \Theta}$, which was to be proved.

The only restriction on this proof is that the number of adatoms be infinitely large, even in whatever small degree of covering may be desired. This requirement is absolutely fulfilled in all cases of practical interest. Thus, for example, in cesium adsorbed on tungsten the concentration of adatoms even when $\Theta = 0.01$ is still very great equals $4.8 \cdot 10^{12}$ per sq. cm (Ref. 2).

Since in our case

$$P_{\text{eff}} = \frac{P_0}{2} - P_1 = \frac{1}{2} P_0^0 - P_1^0 - \left(\alpha + \frac{\beta}{2}\right) E(\Theta), \tag{21}$$

by substituting this expression into (17) and selecting an appropriate $E(\Theta)$, we will obtain $\Delta\delta(\Theta)$ for the case of unlocalized and localized adsorption, respectively:

$$\Delta\varphi (\Theta) = -4\pi n_1 \Theta \left\{ \frac{P_0^0}{2} - P_1^0 - \left(\alpha + \frac{\beta}{2}\right) \frac{(\bar{C}_0 P_0^0 - \bar{C} P_1^0)\Theta^{\frac{3}{2}}}{a_1^2 f (1 + \bar{b}\Theta^{\frac{3}{2}})} \right\}, \tag{22}$$

$$\Delta\varphi (\Theta) = -4\pi n_1 \Theta \left\{ \frac{P_0^0}{2} - P_1^0 - \left(\alpha + \frac{\beta}{2}\right) \frac{(C_0 P_0^0 - C P_1^0)\Theta}{a^3 f (1 + b\Theta)} \right\}. \tag{23}$$

If in these expressions we set $\beta = 0$ or $P_0^0 = 0$ and $\beta = 0$, we will obtain $\Delta\phi(\Theta)$ for the De-Boer or Langmuir model.

Comparison of Theory and Experiment

A comparison of theory and experiment requires a knowledge of a number of independent theoretical parameters. There are five of these parameters —

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namely d_{00}, α, β, γ, and n_1. (Here d_{00} is the distance of an adatom from

the surface if no forces act on it.) The rest are derivatives of them.

If it is assumed that there are no electrical fields on the metal sur-

face, except the mirror-image force field, then parameters d_0 and P_1^0 are

easy to determine by using the expressions

$$d_0 = d_{00}\left(1 - \frac{\mathscr{E}_0}{2\gamma e d_{00}}\right), \quad P_1^0 = \frac{\gamma e d_{00}\alpha}{4d_{00}^3 - \alpha}, \quad \mathscr{E}_0 = \frac{2\gamma e d_{00}}{8d_{00}^3\left[1 - \frac{\alpha + \beta}{4d_{00}^3}\right]}. \tag{24}$$

It is calculated here that $P_1^0 = \alpha\mathscr{E}_0$. The rest of the parameters are

found from the expressions $P_0^0 = 2\gamma e d_0$, $a = (n_1)^{-\frac{1}{2}}$; b, and f are found

from (9). If d_{00} is made identical with the adatom radius and α with

its polarized state, the major portion of the independent parameters can

be known before experimentation.

The Cs-W system. In the case of the Cs-W system (a single-charged

ion of cesium on a tungsten surface) there is no apriori knowledge of

only the single parameter β. The other parameters have the values d_{00} =

= $1.65 \cdot 10^{-8}$ cm, $\alpha = 2.46 \cdot 10^{-24}$ cm^3, $n_1 = 4.8 \cdot 10^{14}$ cm^{-2} (Ref. 2), and $\gamma = 1$.

We have assumed that $\beta = \alpha$. This is, generally speaking, not far from

the truth, since the polarity of dipole P_0 is in a substantial measure

determined by adatom polarity. Figure 3 shows the $\Delta\phi(\theta)$ and $\delta q(\theta)$ curves

(curve 2) computed by means of (23) under this assumption, and the experi-

mental curves from (Refs. 1 and 2) (curve 1).   As is evident from the

figure, the theory which employs only apriori parameters for $\theta \lesssim 0.5$

is not only qualitatively, but also numerically in entirely satisfactory
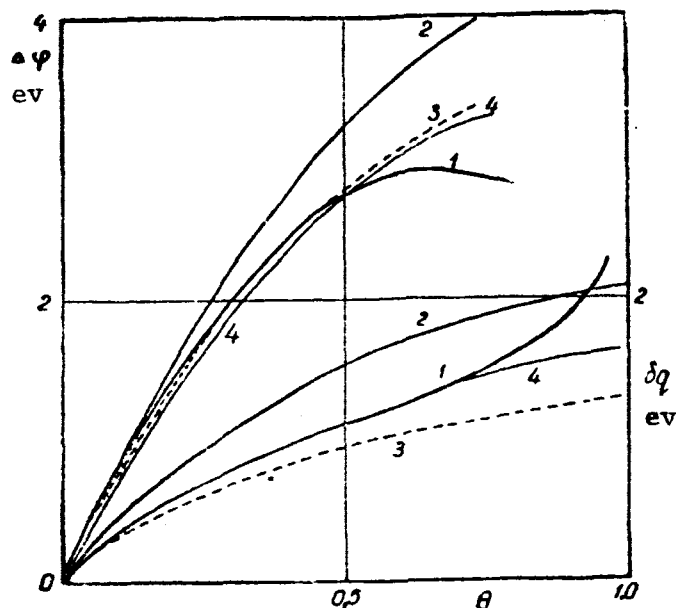
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Figure 3

agreement with experiment. We can readily determine that the De-Boer

model with the above-given parameters drastically diverges from experi-

ment numerically. To obtain satisfactory agreement between the calcula-

tions for this model and experiment, values of α must be taken which   /742

are twice as great as the degree of polarity of the cesium ion. It is

similarly easy to ascertain the unsuitability of Langmuir's model.

The Ba-W system. Unfortunately, the degree of polarity α for the

single-charged barium ion ($\gamma = 1$) is unknown. It is, therefore, necessary

to find the values of the two parameters α and β. On the condition that

$\alpha = \beta$, they proved to equal $2.5 \cdot 10^{-24}$ cm^3. The rest of the parameters,

as is known, are $d_{00} = 1.53 \cdot 10^{-8}$ cm, $n_1 = 5 \cdot 10^{14}$ cm^{-2} (Ref. 14). Figure

4 gives those computed from (23) and (16), and the experimental relationships

for $\Delta\phi(\Theta)$ and $\delta q(\Theta)$. It is evident that when $\Theta \lesssim 0.5$, the agreement between calculation (curves 2) and experiment (curves 1) is quite satisfactory. The $\Delta\phi(\Theta)$ and $\delta q(\Theta)$ curves (curves 3) computed for the De-Boer model ($\alpha = 4.5\cdot10^{-24}$ cm^3) are also included. It is evident that the numerical agreement between calculation and experiment is somewhat worse. The same figure includes the same curves (curves 4) for Langmuir's model computed with the value of $\alpha = 9\cdot10^{-24}$ cm^3, which was wrong in advance since for the Ba atom $\alpha = 60\cdot10^{-24}$ cm^3 (Ref. 15). It is apparent that in this case there is no agreement between theory and experiment.

We also computed $\Delta\phi(\Theta)$ and $\delta q(\Theta)$ for the double-charged barium ion, but the results obtained diverge sharply from experiment. In our opinion, therefore, it must be concluded that barium is adsorbed like a single-charged ion.

The BaO-W System. A comparison of theory with experiment for the case of the BaO-W system is substantially harder to make since every parameter, including n_1 (Ref. 16), is practically unknown for this system. The situation is further complicated, moreover, by the presence on an intrinsic dipole moment in the BaO molecule. We will therefore merely limit ourselves to certain observations. It may be assumed that adsorption of BaO on tungsten occurs in two ways: Either the dipole molecules orienting themselves in the special field of the metal additionally enter into electronic interaction with the latter in such a way that the molecule becomes a negative ion, or the intrinsic dipole moment plays no role and the BaO molecules on the surface take on a
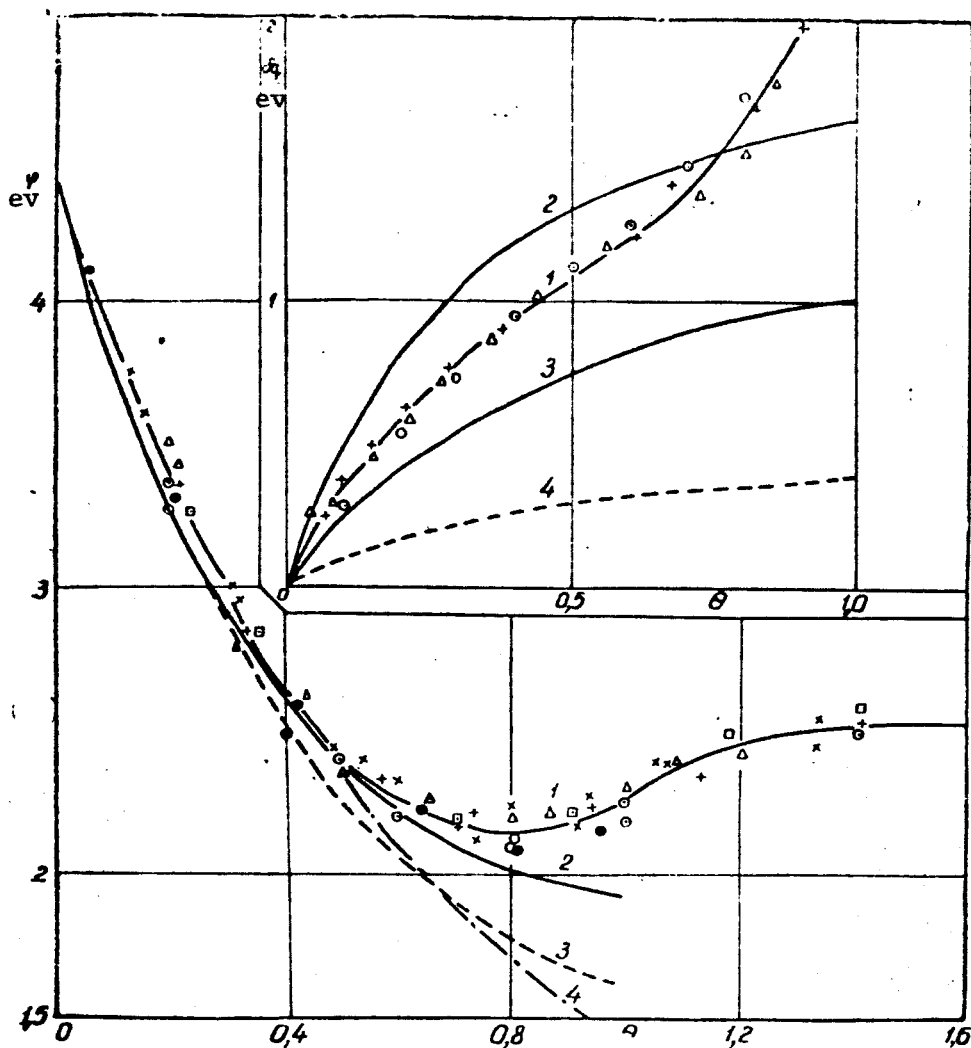
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Figure 4

positive charge. It seems to us, however, that additional data are
necessary to explain this matter, e.g., the value of the intrinsic
dipole moment of the molecule, its polarity, degree of ionization, as
well as the polarity of its positive or negative ion must be known.

Calculating Interaction of Adatoms Which Approach
Each Other at Distance Less Than a

A comparison of theory with experiment has shown that, when $\theta \lesssim 0.5$, (16) in the case of localized adsorption quite adequately describes the relationship $\delta q(\theta)$. This expression is both qualitatively and numerically similar to the empirical first term of (1) which we chose in (Ref. 1). When $\theta > 0.5$, the qualitative divergence of (16) from experiment is apparent, since we derived this expression without taking into consideration the interaction of adjacent adatoms which have approached each other at a distance less than a as a result of random distribution. In fact, in the case of localized adsorption the adatoms are distributed over potential holes in accordance with Boltzmann's law. Therefore, the separate particles may, generally speaking, be found at distances less than a /744 from each other; this can lead to a more intense exchange in heat than follows from (16).

This may be most precisely computed by the method worked out by Miller (Ref. 13), but Miller's theory requires rather laborious numerical calculations if it is to be compared with experiment. Therefpre, we made the computations by Wang's method (Ref. 17), which, although less precise, nevertheless leads to a simple expression.

Let us assume that the adparticles can approach each other within a certain distance x. Energy v of interaction between the particles in such a "pair" inherent to a single particle will designate the probability of "pair" formation. This probability (Ref. 18) equals

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$$\Theta = \frac{\eta\varepsilon}{1 + \eta\varepsilon}, \qquad (25)$$

where $\eta = e^{-\frac{V}{kT}}$, and we find ε from the equation $\frac{\Theta}{1-\Theta} = \frac{\varepsilon(1+\eta\varepsilon)}{1+\varepsilon}$. In

the case where all the adatoms in the film are found at distance x from

each other, every particle will interact with four neighbors (square

lattice). If the degree of covering is Θ, the number of "pairs" will be

$$N = \frac{1}{2} 4n_x \left[\Theta - \frac{1 - \{1 - 4(1-\eta)\Theta(1-\Theta)\}^{\frac{1}{2}}}{2(1-\eta)} \right], \qquad (26)$$

where n_x is the number of adatoms in the whole film with lattice constant

x. Energy U of N "pairs" equals NV, hence

$$\delta q(\Theta) = \frac{\partial U}{\partial(n_1\Theta)} = 2V \frac{n_x}{n_1} \left[1 - \frac{1 - 2\Theta}{\{1 - 4(1-\eta)\Theta(1-\Theta)\}^{\frac{1}{2}}} \right]. \qquad (27)$$

In the case of a square lattice, it may happen that $x = \frac{a}{\sqrt{2}}$ (localized

adsorption), i.e., the adatoms may approach each other at a distance

equal to $\Theta = 2$. Then the variable Θ must be replaced by $\frac{\Theta}{2}$, and we must

set $n_x = 2n_1$. The expression for $\delta q(\Theta)$ will in this case assume the

form

$$\delta q(\Theta) = 4V \left[1 - \frac{1 - \Theta}{\{1 - (1-\eta)\Theta(2-\Theta)\}^{\frac{1}{2}}} \right]. \qquad (28)$$

But we know that a "monolayer" film with $\Theta = 2$ does not exist, since

the energy of interaction of an adatom with its neighbors and with the

rest of the adatoms when $\Theta = 2$ is such that the adatom is ejected into

another layer. It may be assumed that ejection into another layer will

also take place in case $\Theta < 2$, if the four nearest neighbors of the

adatom in question are located at a distance of $\frac{a}{\sqrt{2}}$. Then it is natural

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to assume that the value 4V for the adatom interaction energy with its four nearest neighbors will be greater than, or equal to, the difference between the heats of adsorption in the first and second layers with an arbitrary degree of covering, i.e.,

$$4V > q_0 - \delta q(\Theta) - q_2(\Theta_2),$$ (29)

where $\delta q(\Theta)$ is defined by expression (16), q_2 is the heat of adsorption /745 in the second layer, and Θ_2 is the degree of covering in this layer.

Since the ejection effect appears only at degrees of covering close to unity, we may in the first approximation set

$$4V = q_0 - q_1 - L,$$ (30)

assuming that $q_0 - \delta q(\Theta) = q_0 - \delta q(1) = q_0 - q_1$ and that the adsorption heat value in the second layer is close to the latent heat of vaporization L of the substance adsorbed from its own crystal. Let us substitute (30) into (28) and take the fact into account that, for example, $(1 - \eta) = 0.99$ for Ba-W; then we will obtain the second term in expression (1) which we empirically selected from (Ref. 1) and which gives a good description of the relationship $\delta q(\Theta)$ when $\Theta > 0.5$.

Therefore, starting from the concepts of a statistical distribution of adatoms on the surface and of electrostatic interaction between the adatoms which have approached each other within a distance less than a, we may in the case of localized adsorption explain the curve of $\delta q(\Theta)$ at large values of Θ $(0.5 < \Theta \leqslant 1)$ (Figures 3 and 4) — namely, a great decrease in adsorption heat for the Ba-W and Cs-W systems — since in this case the difference between the adsorption heats in the first and

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second layers is great. The practical absence of such a reduction for the

BaO-W system may also be explained, since in this case this difference

is even negative (Ref. 1).

Hence the change in adsorption heat with the change in Θ, observed

in experiment, must be described by the sum of expressions (16) and (28).

The first describes $\delta q(\Theta)$ which results from the electrostatic interaction

of the adatoms which are randomly distributed in potential holes, but are

unable to approach each other within a distance less than a. The second

expression describes the $\delta q(\Theta)$ which results from the interaction of

adatoms which have approached each other within a distance less than a.

Number of Atoms or Molecules in a Monomolecular Layer

The above considerations may be used for formulating a criterion for

defining the number of adatoms or molecules in the monomolecular layer

per square centimeter of surface. Ordinarily (Refs. 6, 12) this number

n_1 is determined starting from the atom's geometrical dimensions, i.e.,

the minimum distance x_m between adatoms in the "whole" film is deter-

mined in this case only by ejection of their electron envelopes. How-

ever, it may happen that electrostatic forces acting at a distance prove to

be so great that they will eject the adatom into the second layer even

before the electron envelopes come into contact. Then the number n_1

will be determined only by the degree of interaction energy of the

adatom with its neighbors and with the rest of the adatoms. Moreover,

since the adatoms are at distance x from each other and the interaction

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energy per adatom is greater than the adsorption heat difference between
the first and second layers, such a film will not exist -- some of the ada-
toms will be ejected into the second layer. On the contrary, if this
energy is less than the difference mentioned, such a film will exist.
Therefore, if x is such that the energy equals the difference in adsorp-
tion heat, then it is the minimum distance x_m between adatoms at which
the film can exist. In the case of unlocalized adsorption x_m = a and
$n_1 = a^{-2}$. In the case of localized adsorption, x_m still does not equal
the constant of the monolayer lattice, since this value must be divisible
by the lattice constant a_s of the substratum, e.g., for a square lattice
if $x_m < a_s$, a = a_s; if $a_s < x_m < a_s \sqrt{2}$, a = $a_s \sqrt{2}$; and so on.

Thus, computation of x_m for the case of localized adsorption requires
the use of (30) after determining 4V by means of (12), computing the
sums of (4) for the four or six nearest neighbors (c' and c_0'), and
setting a = x_m. Moreover, in (16) for q_1 it is also necessary to replace
a by x_m. Then to find x_m we will derive the equation

$$\frac{(P_0^0 - 2P_1^0)(C_0P_0^0 - CP_1^0)\left[2 + \frac{C\alpha + C_0\beta}{x_m^3 f}\right]}{4f\left[1 + \frac{C\alpha + C_0\beta}{x_m^3 f}\right]^2 x_m^3} + \frac{(P_0^0 - 2P_1^0)(C_0P_0^0 - C'P_1^0)}{4f\left(1 + \frac{C'\alpha + C_0\beta}{x_m^3 f}\right)x_m^3} = q_\bullet - L. \quad (31)$$

From expression (31) it may be deduced that the greater the value of q_0,
the more compact the monolayer is, and, conversely, the greater the value
of L, the more attenuated is this monolayer.

A criterion may be formulated on the basis of the above for deter-
mining the number of adatoms in the monolayer. If the forces of

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electrostatic interaction between adatoms are great, then the minimum interadatom distance x_m is found from (31). If, however, these forces are so small that x_m is less than the size of an adatom, then n_1 is found from purely geometrical considerations.

We employed (31) to compute x_m for Ba-W and Cs-W. For cases of quadratic and hexagonal lattices, respectively, these values proved to be $4.3 \cdot 10^{-8}$ and $4.5 \cdot 10^{-8}$ cm for Ba-W, and $5.0 \cdot 10^{-8}$ and $5.2 \cdot 10^{-8}$ cm for Cs-W. We can see that these values are far greater than the adatom diameters (3.06 and 3.3 angstroms). Starting from the values of x_m, we can determine the number of atoms n_1 in the monolayer per square centimeter of the different faces of a single crystal of tungsten. The table gives the computed values of n_1 for four faces for Ba-W and Cs-W in the case of localized adsorption, as well as the value of A, which is the ratio of n_1 to the number of tungsten atoms in the monolayer for the given face. It is clear from the table that adatom concentration n_1 is not the same on different faces. In the case of Ba-W, the greatest number of them is contained on the (111) face and the least on (112).

Taylor and Langmuir (Ref. 2) experimentally determined the value of n_1 for Cs-W. It was found to equal $4.8 \cdot 10^{14}$ cm^{-2} for the apparent surface of polycrystalline tungsten. Langmuir, starting from the assumption that the tungsten surface is formed by (110) faces and from the geometrical dimensions of the Cs atom, came to the conclusion that the monolayer must contain $3.56 \cdot 10^{14}$ cm^{-2} atoms. Therefore, he was obliged to assume that tungsten surface roughness is 4.8:3.56 = 1.35. As Herring and Nichols

TABLE

System	Face							
	(110)		(111)		(112)		(100)	
	$n_i \cdot 10^{-14}\, cm^2$	A	$n_i \cdot 10^{-14}\, cm^2$	A	$n_i \cdot 10^{-14}\, cm^2$	A	$n_i \cdot 10^{-14}\, cm^2$	A
Ba—W	4,72	1:3	5,8	1:1	4,07	1:2	5.0	1:2
Cs—W	3,56	1:4	1,93	1:3	4,07	1:2	2,5	1:4
Θ_f	0,352		0,089		0,343		0,254	

showed (Ref. 19), however, the surface of polycrystalline tungsten is chiefly composed of faces of four types -- (110), (112), (100) and (111), (113), (116). They ascertained the relative portions Θ_f of the surface occupied by the respective faces (see last column of table). If advantage is taken of these findings, as well as of the tabular data, and the average value of n_1 is computed, it is found to be $3.47 \cdot 10^{14}\ cm^{-2}$, i.e., it happens to be almost equal to the number of adatoms on face (110). When comparing theory with experiment, we also took the fact into consideration that $n_1 = 4.8 \cdot 10^{-14}\ cm^{-2}$. If we carry out the computation assuming that $n_1 = 3.5 \cdot 10^{14}\ cm^{-2}$, we shall obtain a still greater agreement between theory and experiment (curves 4 in Figure 3).

For the Ba-W system, the value of n_1 for a rolled tungsten strip was experimentally determined by us (Ref. 14). It was found to be $5 \cdot 10^{14}\ cm^{-2}$. From the data compiled in the table it follows, however, that such a concentration is possible only for face (100). This does not contradict our assumption (Ref. 1) that the initial texture (100)

of the strip is not completely destroyed.

Conclusions

This paper formulates a theory for the interaction of atoms adsorbed on a metal surface. Its basis is the assumption that this interaction is electrostatic in nature. Calculations are made for three adsorption models: Langmuir's model (polarized atom on metal surface), De-Boer's (polarized ion on metal surface forming a hard dipole together with its mirror image), and the general model proposed by the author (polarized ion forming a soft dipole together with its mirror image) covering both of the preceding models. Formulas are derived for all three models to calculate the change in heat of adsorption $\delta q(\theta)$ and the change in the work function which changes with degree of covering $\Delta\phi(\theta)$. A criterion and a formula for determining the number n_1 of adatoms in the monolayer per square centimeter of surface are proposed. A calculation is also made of the interaction of adatoms which approach each other within a distance less than the lattice constant of the monolayer, which gives both a qualitative and numerical explanation of the course of $\delta q(\theta)$ when $\theta > 0.5$. Theory and experiment are compared for the Ba-W and Cs-W systems. The author's model proved to be the only one to yield good agreement. Agreement was worse for De-Boer's model, while Langmuir's model is altogether unsuitable for describing adsorption of Ba and Cs on W. It was for the latter model that Roberts and Miller (Refs. 7, 13) formerly carried out calculations of $\delta q(\theta)$. On the basis of these calculations, the now generally accepted conclusion was drawn that the

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electrostatic interaction of the adatoms on the surface cannot explain

the experimentally observed values of the change in adsorption heat with

a change in Θ. Therefore, this conclusion is associated only with the

poorly selected model for the phenomenon. With proper model selection,

this conclusion becomes invalid. The good agreement of the experimentally

derived relationships $\Delta\phi(\Theta)$, $\delta q(\Theta)$, and the findings for n_1 for the Ba-W

and Cs-W systems, with the experimental measurements shows that electro-

static interaction of adsorbed atoms is rather substantial. It may be

that it is decisive for the phenomena examined by the author.

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